Bakerian Lecture.—"Further Experiments on the Action exerted by certain Metals and other Bodies on a Photographic Plate." By W. J. Russell, Ph.D., V.P.R.S. Received February 10,—Read March 24, 1898.

In a paper read before this Society in June last* it was stated that certain metals, alloys, and other substances such as picture copal, printing ink, straw board, &c., were able to act even at a distance on a sensitive photographic plate, producing effects similar in appearance and developed in the same way as plates which had been acted on by ordinary light. At that time sufficient experimental evidence had not been obtained to determine the nature of this action, or even to clearly indicate its general character, whether in fact the action arose from vapour given off by the active body, or whether phosphorescence was produced which acted on the plate. That bodies so slightly volatile as zinc, aluminium, nickel, &c., should be able to give off at ordinary temperatures in a few days sufficient vapour to act strongly on a photographic plate, and that such vapour should be able to pass rapidly through media, such as gelatin, celluloid, collodion, &c., seemed difficult to realise, although many of the earlier experiments appeared to indicate that this was the kind of action which took place. Later experiments confirm the view that a vapour is given off, which is the cause of the action on the plate.

Certain organic bodies, as well as metals, have been shown to act on the photographic plate, and in endeavouring to ascertain the nature of this action experiments with organic bodies were first undertaken, as the results which they yield are more easily and rapidly obtained than those with the metals, and if their mode of action was determined it would probably throw light on the action exerted by the metals. In the former communication it was stated that printing ink and copal varnish are active substances, both when in direct contact with a photographic plate and when at a distance from it. Further it was found that the action which they exerted was able to pass through different media. Although printing inks and copal varnishes may vary considerably in composition, the main constituents are constant, hence it was easy to determine that boiled oil and turpentine were the bodies to which they owed their activity, and that these bodies separately behaved in the same way as did printing ink and copal varnish. Boiled oil—that is, linseed oil which has been heated with oxide of lead—is an active substance, and most of the following experiments have been made

* 'Roy. Soc. Proc.,' vol. 61, p. 424.

with the pale drying oil which is prepared by Messrs. Winsor and Newton. Pure turpentine is also a very active substance, and, owing to its volatility, in many experiments very useful. These bodies can be used either as liquids in small dishes or by saturating Bristol board or other neutral and porous bodies, such as ignited pumice stone, &c., with them. In the case of the drying oil it can be painted on glass or cardboard and allowed to harden.

The experiments described in the former communication have been repeated under the same and under slightly different conditions and in another laboratory; the results obtained with one exception confirm the previous statements. Glass, selenite, mica, even in very thin layers, are absolutely opaque to the action, whereas gelatin, celluloid, collodion, guttapercha tissue, tracing paper, parchment, and paper are more or less transparent. Linseed oil and turpentine may fairly be taken as typical examples of active organic bodies. This property of acting on the photographic plate is far from belonging to all volatile organic bodies; for instance, although vegetable oils have the power of acting, mineral oils, so far as they have been tried, have not the power. Benzene, carbon disulphide, chloroform, &c., also are without this power of acting on the photographic plate; but the question of what substances are and what are not active will be dealt with on another occasion; at present it is simply to consider the conditions under which linseed oil and turpentine act on the photographic plate. The picture copal varnish which was much used in the former experiments obviously owes its activity to the turpentine and the oil it contains. Warm the varnish for some length of time, these bodies are driven off and an inactive gum remains. This experiment obviously suggests a vapour as the cause of the action; at the same time would such a vapour pass through bodies such as gelatin, celluloid, &c.? With regard, for instance, to the thin-sheet gelatin, it appears to offer but very slight obstruction to the action of these organic bodies; if the thickness of the gelatin be increased still the action takes place, only the time of exposure has to be considerably longer.* Another striking fact with regard to this emanation from these active bodies is that it gives an accurate picture of the surface from which it has come. A hard copal surface on glass will give a picture showing every brush mark, unevenness, and scratch on the surface, and if the action take place through a thin sheet of gelatin, or even as many as six or more sheets, still the picture of the scratches is distinct. The following experiments are apparently strong evidence that the action on the photographic plate is due to the vapour given off from these organic bodies.

A piece of Bristol board saturated with drying oil, or a piece of

* The thin gelatin is 0·02 mm. and the thick 0·16 mm. in thickness.

glass painted with it or with picture copal, is placed on the bottom of an ordinary plate box and a photographic plate larger than the active body is suspended above it with the film upwards; light is excluded from the box, and the arrangement is left for, say, a fortnight, then the plate when developed will be found to have been acted on irregularly round its edge, at some parts considerably more than at others, but everywhere shading off and evidently in the way which would occur if a vapour had rolled round the edge. Another experiment which showed this kind of action very satisfactorily was carried out as follows:—A circular piece of the Bristol board was saturated with drying oil, and at a little distance above it a smaller circle of mica, which is perfectly opaque to the action, was placed, and again above this was another piece of mica with a circular hole smaller than the circular mica plate, and then the photographic plate was placed above. By this arrangement no direct action could take place between the drying oil and the sensitive plate, but a vapour could work its way between the mica plates and thus reach the photographic plate; and this it did, for after an exposure of three days, on developing the plate there was a dark ring formed shading off towards the centre. Another and very simple experiment illustrating this same point is to place a small circular glass dish, with some drying oil in it, in the middle of a photographic plate, and leave it there for a week. On developing the plate it will be found that no action has taken place where the dish stood, but that immediately beyond the outside of the dish much action has occurred, and that the darkening gradually fades away. There is still another way in which the action of these organic bodies has been tested, and that is by transferring the active power of these bodies to a neutral substance. If vapour be the immediate cause of the darkening of the photographic plate, then it would be possible, if a piece of Bristol board were suspended above drying oil, for instance, for the inactive board to take up those vapours and become photographically active. This was found to take place. Bristol board of good quality is a very useful substance in all these experiments, both as a screen and as an absorbent. It is in itself an inactive body, and may be heated in a water bath before using, to prevent the accidental presence of any substance which might act on the plate. If a piece of the Bristol board be suspended above drying oil, in the liquid or solid state, or turpentine or picture copal for two or three days, or even less, it becomes strongly active, and when placed in contact with a photographic plate quickly darkens it. This action of the Bristol board is well shown if a pattern be stamped upon it, which is easily done by pressing against it a piece of white net (black net must not be used as it is slightly active), then the charged Bristol board will give an unmistakable picture. If turpentine be the active sub-

stance used to charge the Bristol board the exposure need only be for a few hours, but if after this charging it be exposed to the air for a day or two, its activity will be found to have gone. There is obviously no visible indication of this activity of the Bristol board, and consequently if a device be cut out on a screen which is placed in front of a sheet of cardboard, or any inactive paper, and it is exposed to turpentine or to oil, or if the vapour of these bodies be in any other way brought in contact with the paper, a dark picture of such device, which is not visible, may be produced. Some unexpected and curious cases of ghostly pictures thus formed have been met with, they are, however, all produced in this way, and need not be described now. The above experiments have been made at ordinary temperatures, but if the temperature be increased the activity of these organic bodies is also greatly increased. High temperatures cannot, of course, be used, but a temperature of 55° C. does not appear to alter the photographic plate. With drying oil—which is one of the most active substances that has been used—it is easy to obtain a picture in thirty minutes at the above temperature. The interesting pictures which in the former communication it was shown could be produced simply by laying a piece of dry wood or the section of the branch of a tree on a plate are produced by the volatile matter contained in the wood. These pictures appear at first sight very accurate and complete, but this is not really so, for some parts of the structure of the wood are not shown and other parts are too strongly developed, depending on the amount of volatile substance present in the different parts. It is, however, very remarkable that so small a quantity of the volatile body as exists in a piece of dry wood should be able to produce a picture; the activity of the wood is increased by the presence of moisture. This property of acting on the photographic plate, possessed by the linseed oil, belongs apparently to the vapour and not to the oil itself, for if a sheet of thin gelatin be placed on a photographic plate, and on it a thick glass ring nearly filled with oil, and over the top of the ring another sheet of gelatin, not in contact with the oil, and another sensitive plate, it will be found that after a week's exposure no action has taken place below the oil, but that a large amount has occurred above it where the vapour has penetrated the upper sheet of gelatin. A similar result is also obtained by simply floating a piece of the thin gelatin on a dish of oil and placing a sensitive plate above. At the sides where the vapour can form and get away there is action on the plate; in the centre there is none.

In addition to glass, mica, and bodies of that kind, the action does not take place through a layer, except it be very thin, of either gum arabic or of paraffin. If a piece of Bristol board or a glass plate has hardened drying oil on it, and be painted over with a strong solution of gum arabic which is allowed to dry, then the delicate

cracking which occurs can be very well shown on a photographic plate.

Pure water does not act on the plate, neither does pure alcohol or pure ether, but the ordinary commercial specimens of the last two bodies do, and often to a considerable extent. Alcohol which produces a dark picture will, after digestion with lime and careful distillation, be entirely inactive, and ether after careful purification also becomes inactive. Moisture, if present, does not affect this result; thus the presence of certain impurities, and they appear to be some of the most common ones, can be readily photographed, and approximately their amount determined by the darkness of the picture formed, so that by this means can be determined whether, for instance, a purification process is working well and whether it has completely done its work. The pictures are easily obtained by placing some of the liquid to be tested in a small glass dish, and a sensitive plate above it. Obviously it is only certain impurities which will be indicated in this way, but the reaction is otherwise of considerable importance, for it gives a simple method of determining what bodies soluble in these liquids, are capable of acting on a sensitive plate. This matter will be treated of in a separate communication.

That the vapour given off by these organic bodies is the immediate cause of the action on the sensitive plate the above experiments seem to show. At the same time it is remarkable that such a vapour should readily pass through media such as gelatin, celluloid, &c., and not by mere absorption, but in such a way as to produce a picture of the surface from which it emanated.

Passing on to the action which certain metals exert on a photographic plate, results have been obtained which are strikingly similar to those just described. Substitute a piece of polished zinc for a piece of Bristol board saturated with linseed oil, and similar effects are produced on a photographic plate; the time of exposure must, however, be longer. Although both magnesium and cadmium are slightly more active than zinc, this last metal is the most convenient one to experiment with, and has been used in most of the following experiments. In addition to the above three metals, nickel, aluminium, lead, and bismuth have the same property, but not so strongly developed, of acting, both when in contact and when at a distance, on a photographic plate. Cobalt, tin, and antimony can also act in the same way, but their action is considerably feebler, and undoubtedly other metals can act in the same way, but require much longer exposure. Mercury, which in the former paper was stated to be the most active of all the metals which had been tried, is now found to be quite inactive; the metal used in the former experiments was impure. This matter will be explained further on.

As so strong a similarity exists between the effects produced by

the above-mentioned organic bodies and the metals, the question which naturally presents itself is, do they also give off a vapour which directly or indirectly acts on the photographic plate? The following experiments show that such an action does probably occur. Zinc which has been long exposed to the air is inactive. An exposure out of doors for only three or four days diminishes very considerably its activity, but covered up in doors after three weeks it will still give a tolerably dark picture. If it has a bright but perfectly smooth surface it is active, but not strongly so; rub the zinc with coarse sand or emery paper, and it is then obtained in its state of greatest activity; the same applies to all the metals. If, when in this condition, any of the active metals be placed in contact with a photographic plate, a beautifully sharp picture of the scratched surface is obtained. The great increase of the fresh metallic surface produced by the rubbing may account for the increase of activity which the scratching produces. If the zinc plate be raised only slightly above the photographic plate, a sharp picture of the scratches is still obtained, and of course as the distance is increased, so is the indistinctness of the picture increased, and at last it fades into a general cloudiness, and in this form the zinc plate can easily be made to act through the distance of an inch or more.

This action of the metals passes through the same media as do the vapours from the organic bodies, and clear pictures can be obtained through sheets of thin gelatin, &c.; in fact what has already been said with regard to the transmission of the activity of the organic bodies applies to the metals; gelatin, both thin and thick, allows the action of the metal to pass through it; celluloid and collodion do the same, and so does gold-beaters skin and tracing paper. Reasoning, then, from this strong analogy between the action of the organic and the metallic bodies, it must be assumed that the above-mentioned metals from a clean surface and at ordinary temperatures give off vapour, and this vapour apparently acts when under the same circumstances in a like manner to the vapour given off by the drying oil. It gives a clear picture of the metal surface from which it arose, and it can permeate the same media as the organic vapours. The remarkably clear pictures of, for instance, a zinc surface, which can be produced through a sheet, or even several sheets, of the thin gelatin proves that the action is not one of mere absorption.

To gain further knowledge on this point and test the porosity of these different media, the power of hydrogen to diffuse through them was tried by cementing specimens of the different substances on glass tubes, which were filled with hydrogen and placed over water. The action is somewhat remarkable, but requires further confirmation. With the thin gelatin ordinary diffusion does not occur, and a hardly, if any, perceptible rise of the water in the tube

occurs on starting the experiment; but on standing for some length of time, two or three days, the water begins to rise, and after a week or more it will stand at a height of four or more inches above the level in the vessel, and there it remains at least for a month or more. With the thick gelatin there is no evidence of any diffusion occurring. Celluloid acts much in the same way as the thin gelatin, a column of water gradually rises and remains there. The action of the guttapercha tissue is to absorb the hydrogen; the diffusion tube completely fills up with water and remains full without showing any tendency to fall for a couple of months, and then the experiment was stopped. With tracing paper diffusion occurs in the ordinary manner, and the same happened in the single experiment tried with gold-beater's skin. That the rise of the water in the diffusion tubes is not owing to a mere absorption of the hydrogen by the gelatin or guttapercha has been proved by placing a considerable quantity of these bodies in a tube sealed up at one end, filled with hydrogen and inverted over water; after several weeks no rise of the water in the tube occurred. The above experiments have been repeated with the same results, but further trials are being made. Possibly the metallic vapour is in a still finer molecular state than ordinary hydrogen, and thus is able easily to permeate a medium which hydrogen can only slowly get through, and air cannot get through. At all events, this may be looked upon for the moment as a working hypothesis.

That the action of the metals like that of the organic bodies is due to a vapour can be demonstrated by experiments exactly similar to those already described. For instance, if the thin mica plates be arranged above a zinc plate, in the way already mentioned, so as to cut off all direct action between the zinc and sensitive plate, a ring of action is produced which can only be accounted for by supposing a vapour present, which has worked its way between the sheets of mica and thus gained access to the photographic plate. Again, a piece of Bristol board can be made active by contact with, or mere proximity to, a piece of polished zinc. A striking instance of this arose in the following way: a piece of perforated zinc had lain on the bottom of an ordinary plate box for a considerable length of time, probably about two months; the zinc was then taken away, and a sensitive plate dropped into its place. On developing this plate, a picture of the perforated zinc was obtained. Other experiments of a similar kind have been made. If the Bristol board be not in direct contact with the zinc; if a screen, with holes cut out in it, be interposed, it will be found that the Bristol board where exposed to the direct action of the zinc will become active, and will give an exact picture of the holes or whatever design it may be which has been cut out on the screen. To produce this effect the

cardboard has to be exposed to the zinc for fully six weeks. This changing of the Bristol board does not take place satisfactorily above ordinary temperatures. With other metals than zinc, these changing effects have not as yet been obtained.

Another experiment, which illustrates the way in which the metals can act, is to take a piece of ordinary perforated zinc, polish one side, and lay this polished side against a plate of plain glass in a printing frame, then place the photographic plate against the dull side of the perforated zinc, and leave it in the dark for three or four days; then, on developing the plate, a reversed picture is obtained, that is, the holes in the zinc will be represented by dark spaces, and the zinc itself by light ones. If the holes in the perforated zinc are large, they are represented by shaded circles, so that these pictures are produced by the vapour emitted by the polished zinc which has crept into the open spaces and thus gained access to the photographic plate. It has already been shown that the action exerted by zinc passes more readily down a glass than down a paper tube of the same size; this has been strikingly confirmed by taking two pieces of glass tubing 1 inch long $\frac{3}{4}$ inch in diameter; inside one a single coil of inactive paper was placed, and both tubes stood on a sheet of polished zinc, and a photographic plate rested on the top of them. They were then left for a week, and on developing the plate, a black patch appeared above the tube without the paper, and no action was visible above the one with the paper. Without removing the paper, it was painted over with melted paraffin, and again a photographic plate put on the top of the two tubes; now two circular dark patches were produced of equal intensity.

If the activity of the zinc depends on a vapour which it emits, it seemed possible that it could be carried along by a stream of air. In order to try whether this was the case, a tube a foot long was packed with zinc turnings which had been amalgamated, and a stream of pure air sent through it. The end of the tube was fixed into the side of a dark box and a sensitive plate with a screen upon it suspended above it, thus no direct action could be exerted by the amalgamated zinc on the plate. The experiment was continued for four days, then, on developing the plate, a picture of the screen above where the tube entered the box was obtained, but at the other end of the plate there was no action.

The presence of mercury in this experiment was unsatisfactory, and might account for the result obtained, therefore an exactly similar experiment was made, and zinc turnings alone were used and a plate without a screen. The experiment was carried on for a week, and it was then found that a black patch had been produced immediately above the end of the tube. To be sure that this darkening did not arise from the action of the air, the whole of the zinc was

removed from the tube and again the air sent through it for a week, the sensitive plate showed no signs of any action having taken place.

To try whether any accumulation of the vapour, and hence an increase of action could be brought about by an increase of zinc surface, two small circular glass dishes were taken, about $1\frac{1}{2}$ inches in diameter and $\frac{1}{2}$ inch in depth; into one a single disc of bright zinc foil was placed, and in the other twenty similar discs, then on the top of both vessels a photographic plate was placed. The single disc was raised on a piece of glass, so both end discs were at the same distance from the plate. The discs were a little smaller than the glass vessels, and, owing to their not being quite flat, there was a space between each one. In two experiments there was no marked difference between the density of the pictures produced, the single disc produced as much effect as the twenty. A more direct way for the passing off of the vapour was then made by cutting a circular hole $\frac{3}{8}$ inch in diameter through the centre of all the zinc discs, and now a very black central spot was formed by the twenty zincs, and of course there was a white spot with the single disc, so that the vapour accumulated to a considerable extent in this central space.

It has already been mentioned that the statement in the former paper that mercury was the most active of the metals is incorrect. The error arose from not suspecting that a trace of any impurity would affect the activity of the mercury, and, consequently, not taking special precautions to insure its perfect purity. On repeating the former experiments with another sample of mercury it was found that no action occurred, which seemed very remarkable; moisture was added, the temperature was increased, but still no action took place; the addition of a little zinc to the mercury was then tried, and it was found that this made the mercury excessively active. The presence of a very small quantity of zinc is able to effect this change, certainly less than 1/300th per cent. It is very remarkable that so small an amount of the metal can cause so strong an action on the photographic plate, for the exposure to the vapour given off by such an amalgam need not, even at ordinary temperature, be longer than two to three days. If other active metals are dissolved in pure mercury they act in the same way, at all events, this applies to magnesium and to lead. If silver, on the contrary, be added it does not render mercury active, nor does sodium. This action of mercury, which contains zinc or lead, the most common impurities, is so readily recognised that it becomes a valuable test for its purity, and a very interesting means of following the effect produced by any purifying process. A specimen of mercury containing not more than 1/300th per cent. of zinc gave a very dark picture; this mercury was then treated first with sulph-

uric acid and afterwards, for three days, with nitric acid, and the picture it then gave was very faint, and on repeating this purifying process no picture at all was produced. Again, a sample of mercury containing zinc was carefully distilled. The distillate gave a very faint but very distinct picture. Another sample of distilled mercury also gave a faint picture.

Temperature, as might be expected, affects greatly this activity of the metals; at 4° or 5° C. zinc has but little action on a photographic plate. Most of the foregoing experiments have been made at about 17° or 18° C., and some, as specially noted, at 55° C. The Ilford special rapid plates have been used.

It appears, then, from the above experiments that certain metals have the property of giving off, even at ordinary temperatures, vapour which affects a sensitive photographic plate, that this vapour can be carried along by a current of air, and that it has the power of passing through thin sheets of such bodies as gelatin, celluloid, collodion, &c., in fact, so transparent are these bodies to the vapour that, even after it has passed through them, it is able to produce clear pictures of the surface of the metal from which it came. That much remains to discover with regard to this action of the metals is obvious, the most active metals are not the most volatile. Nickel is very active, cobalt only very slightly so, copper and iron are practically inactive. I hope before long to be able to bring before the Society further developments of these curious actions, both of metals and organic bodies.

The foregoing experiments have been made in the Davy-Faraday laboratory, and I beg to thank the managers of the Royal Institution for having allowed me to work in their laboratory. My thanks are also due to my assistant, Mr. Block, for the very careful and intelligent way in which he has aided me with the experiments.

March 24, 1898.—Additional experiments have been made with active organic substances, in order to determine to what class of bodies they belong. As already stated, linseed oil and turpentine were the two substances first found to be very active organic bodies, and following out these results it has been proved that vegetable oils in general have more or less this property of acting on a photographic plate. Linseed oil, for instance, is very active, olive oil only very slightly so. Even samples of "pure" linseed oil obtained from the different artists' colourmen vary considerably in the amount of action which they exert. The boiled, or drying linseed oil, has, at ordinary temperatures, the same activity as the ordinary oil, but under other conditions it appears there is some difference in their action. Another class of bodies, also called oils, namely the essential oils, have been found to be very active substances.

Samples of commercial specimens of the following essential oils have been tried:—Peppermint, lemons, pine, juniper, bergamot, winter green, lavender, cloves, eucalyptus, cajeput, and cedrat, and were all found to be active, and not only when used by themselves, but also when dissolved in a large amount of pure alcohol. It is well known that the active substances in the essential oils are bodies known as terpenes, and I have to thank Dr. Tilden for supplying me with pure specimens of these bodies; they are all of them remarkably active. Paraldehyde and benzaldehyde are also very active bodies. Ordinary aldehyde and formaldehyde, as they have been at present applied, are only slightly active. Guaiacum, both when in powder and in alcoholic solution, is active, and so are powdered cinnamon, sweet spirits of nitre, and eau de cologne. Brandy is slightly so. Now the important property belonging to all these bodies is their reducing or oxygen-absorbing power, hence the conclusion that it is this property which enables them to act on the photographic plate. The mineral oils, purified petroleum spirit, aloohol, ether, the esters, such as ethyl acetate, benzene, nitrobenzene, are all, when pure, unable to produce any effect on a sensitive plate, and even oxidised bodies nearly related to the terpenes, such as terpinol and camphor, are not active, neither is thymol. Terebene is an exceedingly active body. The difference of activity of the ordinary oils seems to follow their oxygen-absorbing power, at all events it is so with regard to linseed and olive oils, for the former is the most active of the oils, and 1 gram of it is said to be capable of absorbing 186 c.c. of oxygen, while the same weight of olive oil can absorb only 8·2 c.c. It is also interesting to note that, at least with some of these active bodies, results can be obtained which correspond to what photographers term solarisation or reversal, the action, when modified, giving a black picture, when carried to its full extent a white one.

It has already been stated that a mere trace of zinc makes mercury active, but it is certainly equally curious and unexpected that a trace of zinc should make alcohol active. It is only necessary to take pure alcohol and place in it some strips of bright zinc foil, leaving the metal in for three or four days. It will then be found that the alcohol can act strongly on a photographic plate. The same happens with ether and with ethylacetate, but not with benzene. In addition to zinc, cadmium, magnesium, aluminium, and fusible metal can act in the same way, whereas lead, nickel, tin, silver, sodium, and, as far as experiments have gone, all the inactive metals, have no such power. This reaction is still being investigated, but certain it is that careful filtration does not remove this activity from alcohol, nor does distillation entirely destroy it.